THE RELATIVE STABILITIES OF SOME MOLECULAR ADDITION COMPOUNDS OF BORON^(I)

W. A. G. GRAHAM* and F. G. A. STONE

Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts

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Abstract—Using boron trifluoride as a reference acceptor molecule, the methyl derivatives of oxygen, sulphur and selenium have an order of electron-pair donor power: O > S > Se. With both borine and trimethylborine, however, the order of co-ordination is S > Se, O. Moreover, the adducts $(CH_3)_2S \cdot BH_3$ and $(CH_3)_2S \cdot BH_3$ are more stable than their boron trifluoride analogues. The weakness of boron trifluoride as an acid was further demonstrated by its quantitative displacement by diborane from the complex $(CH_3)_2 P \cdot BF_3$. In Group Vb the order of co-ordination of methyl derivatives towards BH_3 is apparently P > N > As > Sb, compared with the order N > P > As > Sb shown by all other Group-IIIb acceptor molecules so far investigated. Possible explanations for these observations are discussed.

1. INTRODUCTION

As a consequence of studies carried out by a number of workers it is now recognized that the electron-donor bonding power of the elements of Groups Vb and VIb does not always decrease with increasing atomic size. This has necessitated a modification of ideas concerning the nature of the bonding in some compounds once thought by most to be satisfactorily described in terms of the classical co-ordinate link. The majority of complexes inadequately described by the lone-pair theory of co-ordination are formed by a few transition metals. However, the chemistry of some of the compounds formed by IIIb elements, and of boron in particular, provides several other examples of unusual relative stabilities, the explanation of which may require applying as many concepts as the modern theory of valence can suggest.

The work described here was carried out in order to extend our knowledge of borine-type adducts, with the special object of preparing compounds likely to display unexpected stability relationships when viewed in terms of what is so far known about order of co-ordination of ligands to IIIb atoms.

Several techniques have been used for the assignment of relative electron-pair donor power of the atoms of Group V and Group VI. The most satisfactory method involves study in the gas phase of the thermal dissociation of the complex. Knowledge of the variation of dissociation with temperature permits thermodynamic constants to be evaluated, and a quantitative measure of the strength of the metal-ligand bond is thereby obtained. It is unfortunate that many complexes are either too stable or too unstable for the application of this method.

Fortunately, for many purposes it is sufficient to establish relative stabilities only qualitatively. The use of displacement reactions supplies this information. Although sometimes complicated by lattice energy and volatility effects, the method has proven

* Present address: Department of Chemistry, University of Southern California, Los Angeles, California.

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useful for the more stable complexes. Furthermore calorimetric procedures have recently been developed for the determination of the heats of formation in solution of molecular addition compounds.⁽²⁾ Of these methods, gas phase dissociation studies and displacement reactions have been the most widely used.

It is important also to note that for complexes of low stability, it has long been customary to infer relative stabilities from relative volatilities. The following rule has been formulated:⁽³⁾ "... of two addition compounds of closely similar structure and molecular weight, the less stable exhibits the higher saturation pressure." For addition compounds differing in molecular weight, it would be expected that the heavier would be the less volatile. If instead the heavier is found to be more volatile, this is taken to indicate that it is also more highly dissociated.

Thus DAVIDSON and BROWN,⁽⁴⁾ using trimethylaluminium as a reference acid in the LEWIS⁽⁵⁾ sense, have examined the stability of the adducts $(CH_3)_3$ N·Al(CH₃)₃, (CH₃)₃P·Al(CH₃)₃,(CH₃)₂O·Al(CH₃)₃, and (CH₃)₂S·Al(CH₃)₃. Furthermore,COATES⁽⁶⁾ has studied the complex (CH₃)₂Se·Al(CH₃)₃, as well as molecular addition compounds obtained by treating the acceptor molecule trimethygallium with the methyl alkyls of Vb and VIb elements.

The experimental results of these workers demonstrated that towards trimethylaluminium stability decreased in the order N > P, and also O > S > Se. With the common electron-pair acceptor trimethylgallium the order of co-ordination to Group-V alkyls was similar, viz.: N > P > As > Sb, but in Group VI the order was $O > Se > S \sim Te$. Both in the case of trimethylaluminium and trimethylgallium, however, oxygen was found to be a better electron-pair donor than sulphur, and nitrogen a better donor than phosphorus. This has been contrasted^(7, 8) with the reverse behaviour of certain transition metals. However, BURG and WAGNER,⁽⁹⁾ made the important observation that $(CH_3)_2S \cdot BH_3$ was more stable than $(CH_3)_2O$ ·BH₃, showing that towards borine the bonding power of sulphur in dimethylsulphide was greater than that of oxygen in dimethylether. The implication of this discovery to the co-ordination chemistry of Group III has been briefly mentioned elsewhere.^(10, 11) Thus in terms of the behaviour of aluminium and gallium towards oxygen and sulphur as donors the behaviour of boron, as borine at least, is anomalous. Since the strength of a ligand-metal bond depends in part on the substituents on both the ligand and the metal we were prompted to prepare a number of new BX₃-type adducts, and re-examine more closely some borine complexes already reported.

2. EXPERIMENTAL

Apparatus and Materials

The work described here was carried out in a high-vacuum system of conventional design. Saturated vapour pressures, and gas phase dissociations of the complexes were studied in a tensimeter.⁽¹²⁾

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Temperatures were measured with vapour-tension thermometers, or by a mercury thermometer calibrated by the National Bureau of Standards. Infra-red spectra were recorded using a Model 21 Perkin Elmer double beam spectrometer, and a 4 cm gas cell. Hydrogen gas formed in a few of the experiments was collected in a gas burette by means of an automatic Sprengel pump. Its purity was checked by ignition over copper oxide at 700°.

The diborane used in this investigation had vapour tensions very close to the values reported in the literature, e.g. 224.7 mm at -111.9° , literature⁽¹³⁾ value 225.0 mm at -111.9° . Trimethylborine was purified through its trimethylamine complex followed by displacement with a deficiency of boron trifluoride. The vapour tension was 85.6 mm at -63.5° ; STOCK and ZEIDLER⁽¹⁴⁾ report the same value at this temperature. The boron trifluoride used had a vapour tension of 305 mm at -111.8° . Of the donor molecules employed in this work, the purification of trimethylamine trimethylphosphine, and dimethylether presented no difficulty and the samples used had vapour tensions in agreement with those reported in the literature. Commercially available dimethylsulphide, however, was treated with a mixture of sodium and copper shot,⁽¹⁵⁾ and then fractionated until a tensimetrically homogeneous sample was obtained with p = 167 mm at 0° (literature⁽⁴⁾ 167 mm). Dimethylselenide was prepared from elemental selenium by the method of BIRD and CHALLENGER⁽¹⁶⁾ In our hands, the method yielded a grossly impure product. The crude dimethylselenide was transferred to the vacuum system, and a tensimetrically homogeneous product was obtained after prolonged treatment with sodium wire.

Analysis gave the following percentage composition: C, 22.08; H, 5.36; Se, 72.49; Theory for $(CH_3)_2$ Se: C, 22.03; H, 5.55; Se, 72.42.

Characterization of Dimethylselenide

Since vapour tensions for this compound do not seem to have been recorded, the observed values are given in Table 1.

t, °C	7	11	15	20	25	30	35	40
P_{mm} (obsd)	99·4	119·9	144·8	180·6	223·5	274·0	333·7	402·8
P_{mm} (calcd)	100·2	120·8	144·5	180·3	222·8	273·5	333·4	403·6

TABLE 1.—VAPOUR TENSIONS OF LIQUID (CH₃)₂Se

The vapour tensions shown in Table 1 determine the equation $\log P_{\rm mm} = 7.747 - 1610/T$, whence one calculates the boiling point as 57.7° and the Trouton constant as 22.2 cal deg.⁻¹ mole⁻¹. The melting point of dimethylselenide was -87.2° (Stock magnetic plunger method).

Preparation and Study of Complexes

Dimethylether-Trimethylborine. Dimethylether was treated with an equal volume of trimethylborine. The volumes in the gas phase at room temperature were found to be additive. Furthermore when the mixture was cooled to -78° the pressure above the liquid was only slightly less (6 per cent) than that calculated using RAOULT's law. It may be concluded that $(CH_3)_2O^{\circ}B(CH_3)_3$ does not form down to -78° .

Dimethylsulphide-Trimethylborine. A 19.6 c.c.* sample of dimethylsulphide was treated with 28.1 c.c. of trimethylborine in the tensimeter. After standing for 12 hours at -78.5° , 8.9 c.c. of trimethylborine were recovered. A white *solid* remained, with inappreciable saturation pressure at -78.5° . The molar ratio of $(CH_3)_2S:(CH_3)_3B$ in the solid is 1.02, corresponding to the complex $(CH_3)_2S:B(CH_3)_3$.

^{*} The term c.c. throughout this paper refers to volumes at S.T.P.

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⁽¹⁴⁾ A. STOCK and F. ZEIDLER Ber. 54, 531 (1921).

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⁽¹⁶⁾ M. L. BIRD and F. CHALLENGER J. Chem. Soc. 570 (1942).

TABLE 2.—SATURATION PRESSURES OF SOLID $(CH_3)_2$ S·B $(CH_3)_3$								
t, °C	69.7	-66·1	-64.4	-61.3	-56.5	54.8		
$P_{\rm mm}$ (obsd)	1.25	1.80	2.20	3.20	5.60	6.90		
$P_{\rm mm}$ (calcd)	1.11	1.77	2.20	3.21	5.68	6.89		

The saturation pressures of the solid reported in Table 2 determine the equation $\log P_{mm} = 11.637 - 2358.5/T$.

Melting of the complex occurred over the range -43° to -41° .

At 24.8° and a pressure of 300.9 mm, the combined volume of the gases was 38.5 c.c., whereas the sum of the volumes of the components was 38.8 c.c. Hence dissociation of the complex in the gas phase is complete.

Dimethylselenide-Trimethylborine. A sample of dimethylselenide (39.9 c.c.) when treated with trimethylborine (39.9 c.c.) formed a white solid at -78° . After several hours at this temperature the pressure was 8.6 mm. At 25.0° C and 97.3 mm, the volume of the mixture reduced to standard conditions was 79.7 c.c., indicating complete dissociation in the gas phase.

Dimethylsulphide-Borine. Saturation pressures observed by us were very close to those already reported by BURG and WAGNER⁽⁹⁾ It was important to verify the saturation pressures in order that the dissociation of the complex be studied well above the condensation point.

A sample of $(CH_3)_2$ S•BH₃ was prepared in the tensimeter by treating dimethylsulphide with exactly half its volume of diborane. The variation of pressure with temperature together with other data are recorded in Table 3. K_p is the equilibrium constant for the reaction:

$$(CH_3)_2 S \cdot BH_3(g) = (CH_3)_2 S(g) + 1/2 B_2 H_6(g).$$

<i>t</i> , ⁰C	$P_{\rm mm}$ (obsd)	$P_{\rm mm}$ (calcd)	α	K_p (atm. ¹ / ₂)	$K_p(\text{atm.}^{\frac{1}{2}})$ (caled)
40.0	37.66	27.20	0.769	0.391	0.390
42.0	38.00	27.37	0.777	0.411	0.411
44.0	38.33	27.55	0.783	0.430	0.434
46.0	38.72	27.72	0.794	0.463	0.456
48.0	39.05	27.89	0.800	0.485	0.480
50.0	39.38	28.07	0.806	0.508	0.505
52.0	39.66	28.24	0.809	0.519	0.530
54.0	40.04	28.41	0.818	0.558	0.556
56.0	40.42	28.59	0.828	0.600	0.583
58.0	40.70	28.76	0.830	0.613	0.612
60.0	41.02	28.93	0.835	0.640	0.641

A check of the dissociation pressures as the sample was cooled showed that no irreversible decomposition had taken place. The variation of K_p with temperature is represented by the equation

log
$$K_p$$
 (atm.¹) = 3.190 - 1127/T; whence $\Delta F_T^2 = 5157 - 14.60T$.

Therefore, for the reaction $(CH_3)_2$ S·BH₃ $(g) = (CH_3)_2$ S (g) + 1/2 B₂H₆ (g), $\Delta H^\circ = 5.2$ kcal.mole⁻¹ and $\Delta S^\circ = 14.6$ e.u.

BURG and WAGNER⁽⁹⁾ reported the degree of dissociation at one temperature, but this is rendered suspect by an error in their calculations. Their data also suggest that dissociation was studied only slightly above the saturation point, a procedure known to lead to error.⁽¹⁷⁾

(17) H. C. BROWN, M. D. TAYLOR, and M. GERSTEIN J. Amer. Chem. Soc. 66, 431 (1944).

Dimethylselenide-borine. Diborane and dimethylselenide reacted in exactly a 1:2 ratio at $-78\cdot5^{\circ}$ to form a white solid, as would be expected for the formation of $(CH_3)_2Se^{\circ}BH_3$. The melting range of the addition compound was -34° to -32° . Saturation pressures of the complex are recorded in Table 4.

t, °C	0.0	10.0	17.0	21.0	25.0	30.0	35.0
P _{mm} (obsd)	51.4	82.0	115.4	138.7	167-2	207.7	256.9
$P_{\rm mm}$ (calcd)	49.0	82.0	115.3	139.0	166·7	208.0	257.0

TABLE 4.—SATURATION PRESSURES OF LIQUID (CH₃)₂Se·BH₃

The saturation pressures shown in Table 4 determine the equation $\log P_{mm} = 8.030 - 1732/T$, whence one calculates the "boiling point" as 63.2° and the Trouton constant as 23.5 cal deg⁻¹ mole⁻¹. When a sample of dimethylselenide-borine was studied in the gas phase over the temperature range 6° to 34°, the pressures observed were within experimental error those expected for complete dissociation.

Dimethylsulphide-boron trifluoride. A 26.5 c.c. sample of dimethylsulphide combined with 26.4 c.c. of boron trifluoride to form a solid at -78.5° , implying the formation of the molecular addition compound (CH₃)₂S•BF₃. The saturation pressures of the liquid are recorded in Table 5. No irreversible decomposition of (CH₃)₂S•BF₃ was observed during the experimental work.

t, °C	0.0	4.0	9.0	14.0	16.0	20.0	25.0
P_{mm} (obsd)	45·5	59·0	82·0	112-6	127·4	163·1	217·2
P_{mm} (calcd)	45·1	59·2	82·0	112-7	127·4	162·2	217·8

TABLE 5.—SATURATION PRESSURES OF LIQUID (CH₃)₂S·BF₃

The results presented in Table 5 correspond to the equation $\log P_{mm} = 9.806 - 2227/T$, implying a "boiling point" of 48.4° and a Trouton constant of 31.6 cal.deg.⁻¹ mole⁻¹.

In a study of the gas-phase dissociation, the extent of dissociation was found to vary from 96.2 to 97.4 per cent over the temperature range 12° to 34° . The observed increase in pressure over this range was 5.31 mm, while the increase expected for an ideal gas was 4.88 mm. This confirms that dissociation, although greater than 95 per cent, is not complete at these temperatures. The sensitivity of the equilibrium constant to the degree of dissociation as the latter approaches unity makes it impossible to obtain a reliable estimate of the enthalpy change for this dissociation.

Dimethylselenide-boron-trifluoride. Dimethylselenide (40.5 c.c.) was treated with boron trifluoride (65.2 c.c.) forming a solid at -78.5° . Subsequently, 25.0 c.c. of pure boron trifluoride was recovered; hence the dimethylselenide: boron trifluoride reaction ratio was just 1 : 1, corresponding to $(CH_3)_2$ Se*BF₃. The saturation pressure of dimethylselenide-boron trifluoride at -45.2° was 48.1 mm, and 398 \pm 2 mm at 0°. The complex was thus considerably more volatile than $(CH_3)_2$ Se*BF₃. Furthermore in the gas phase at room temperature $(CH_3)_2$ Se*BF₃ was found to be completely dissociated, the variation of pressure with temperature corresponding to that expected for an ideal gas.

Relative Stabilities of Some Complexes

The relative stability of a number of addition compounds was established by the following displacement reactions:

1. $2(CH_3)_2 S \cdot BF_3 + B_2 H_6 = 2(CH_3)_2 S \cdot BH_3 + 2BF_3$

A 7.8 c.c. sample of dimethylsulphide-boron trifluoride was prepared, and to this 3.3 c.c. of B_2H_6 was added. The mixture was equilibrated in a U-trap at -23° for one hour. The contents were then distilled from the -23° trap through a second trap at -140° into a third trap at -196° . The volume of the gas passing -140° was 5.8 c.c., which on hydrolysis yielded 3.4 c.c. of hydrogen; hence the 5.8 c.c. comprises 0.6 c.c. diborane and 5.2 c.c. boron trifluoride. The reaction proceeded, therefore, about 80 per cent to the right.

2. $2(CH_3)_3P \cdot BF_3 + B_2H_6 = 2(CH_3)_3P \cdot BH_3 + 2BF_3$

In a typical experiment, freshly sublimed trimethylphosphine-boron trifluoride (30.3 c.c.) was heated with diborane (10.6 c.c.) in a 500-ml bulb at 80° for 22 hours. After cooling to room temperature the bulb was frozen at -196° and attached to the vacuum line through a tube opener. The bulb was opened and it was observed that no substance was present with a finite vapour pressure at -196° . This indicated no hydrogen had been formed during the heating by the destruction of BH₃ groups. The bulb was warmed to room temperature and 20·1 c.c. of gas was recovered after passage through a trap at -78.5° ; the latter was intended to condense any complex which sublimed during the recovery of more volatile materials.

The infra-red spectrum of the recovered gas was identical with that of pure boron trifluoride. When the gas was heated with water in a sealed tube, no hydrogen was formed, showing that diborane had not been present.

It may be concluded that the reaction proceeded quantitatively to the right, with displacement of boron trifluoride by diborane.

3. $(CH_3)_3P \cdot BF_3 + (CH_3)_3N = (CH_3)_3N \cdot BF_3 + (CH_3)_3P$

A 32·2-c.c. sample of trimethylphosphine-boron trifluoride was heated with 32·0 c.c. of trimethylamine in a 500-ml bulb at 80° for 22 hours. After cooling to room temperature, the bulb was frozen at -196° and opened to the vacuum system. No hydrogen had been formed. The bulb was warmed to room temperature and 31·0 c.c. of gas was recovered after passage through a trap at $-78\cdot5^{\circ}$.

The infra-red spectrum of the recovered gas was identical with that of pure trimethylphosphine. The vapour pressure of the gas was $165 \cdot 3 \text{ mm}$ at 0° , and that expected for pure trimethylphosphine is 161 mm. Since the vapour pressure of trimethylamine at 0° is $680 \cdot 5 \text{ mm}$, only a very small amount of this substance could be present. These results show that the reaction has proceeded quantitatively in favour of $(CH_a)_3 N \cdot BF_a$ with displacement of trimethylphosphine by trimethylamine.

4. $2(CH_3)_3N \cdot BF_3 + B_2H_6 = 2(CH_3)_3N \cdot BH_3 + 2BF_3$

A 32·1-c.c. sample of trimethylamine-boron trifluoride was sealed up with 22·2 c.c. of B_2H_6 in a 500-ml bulb, which was heated for 12 hours at 80°. The only volatile products were 1·92 c.c. of hydrogen and 21·3 c.c. of unchanged diborane. The infra-red spectrum of the condensable gas showed no absorption in the 750-cm⁻¹ to 650-cm⁻¹ region, where boron trifluoride absorbs strongly. These results show that diborane does not displace boron trifluoride from trimethylamine under the conditions used.

5. $(CH_3)_3N \cdot BH_3 + (CH_3)_3P = (CH_3)_3P \cdot BH_3 + (CH_3)_3N$

A 28.2-c.c. sample of trimethylamine-borine was heated with 28.3 c.c. of trimethylphosphine in a 500-ml bulb at 120° for four days. The reaction bulb was cooled to room temperature and attached to the vacuum system where the volatile products were examined. No hydrogen was present, indicating that no pyrolysis of borine groups had occurred. The volume of the gas recovered, after passage through a trap at -78.5° , was 27.5 c.c. The weight of this gas was 76.6 mg, implying a molecular weight of 62.4; trimethylamine requires 59.1, trimethylphosphine 76.1.

The infra-red spectrum of the gas was consistent with a mixture of trimethylamine and trimethylphosphine, and from the molecular weight, the amounts of these gases are estimated as 22.2 c.c. and 5.3 c.c. respectively. These figures imply that the reaction has proceeded eighty per cent to the right. To put this important conclusion on a firmer basis, a method of analysis was devised for the mixture. This is based on the fact that trimethylphosphine reacts with carbon disulphide to form a nonvolatile substance, whereas trimethylamine does not react at all.⁽¹⁸⁾ Application of the method to mixtures of trimethylamine and trimethylphosphine of known composition established its accuracy. The 27.5-c.c. sample recovered from the above reaction was then treated with 83.3 c.c. of carbon disulphide in a trap so that a liquid phase was always present; this is important, as the reaction is rapid in the liquid phase but extremely slow in the gas phase.⁽¹⁸⁾ The reaction is complete if no more red solid forms when the mixture is transferred to a clean trap. The volume of recovered gases, consisting of trimethylamine and excess of carbon disulphide, was 99.4 c.c. Treatment with 34.1 c.c. of boron trifluoride removed trimethylamine as its very stable complex, $(CH_a)_a N \cdot BF_a$. The remaining 12.2 c.c. of boron trifluoride was separated by distillation through a trap at -140° , where 77.6 c.c. of carbon disulphide were retained. These results show that the original mixture consisted of 21.9 c.c. of trimethylamine and 5.7 c.c. of trimethylphosphine, in good agreement with the composition expected from its molecular weight.

That the equilibrium was in favour of trimethylphosphine-borine and trimethylamine was confirmed by heating trimethylamine with $(CH_a)_3P\cdot BH_a$ when it was found that reaction 5 proceeded to the left to the extent of about 25 per cent.

3. DISCUSSION

By analogy with its behaviour towards trimethylaluminium and trimethylgallium, trimethylamine should form a more stable compound than trimethylphosphine with boron trifluoride. Available data confirm this expectation. Thus the compound trimethylamine-boron trifluoride shows no dissociation into its components at temperature as high as 177° .* Trimethylphosphine-boron trifluoride would be extensively dissociated at this temperature.⁽¹⁹⁾ In agreement with these facts, we found that the displacement reaction:

$$(CH_3)_3P \cdot BF_3(s) + (CH_3)_3N(g) = (CH_3)_3N \cdot BF_3(s) + (CH_3)_3P(g)$$

went quantitatively to the right.

The adduct trimethylarsine-boron trifluoride does not appear to have been described but it is reasonable, in view of the existence of phosphine-boron trifluoride and the nonexistence of arsine-boron trifluoride,⁽²⁰⁾ to expect the stability order:

$$(CH_3)_3N \cdot BF_3 > (CH_3)_3P \cdot BF_3 [> (CH_3)_3As \cdot BF_3],$$

where the brackets indicate a tentative but very reasonable conclusion.

Considering next the behaviour of Group-VI elements towards boron trifluoride, it was found by us that dimethylsulphide-boron trifluoride was more than 95 per cent dissociated into its components at room temperature and 65 mm pressure. The thoroughly characterized complex dimethylether-boron trifluoride is less than 20 per cent dissociated under similar conditions.⁽²¹⁾ Dimethylselenide-boron trifluoride was found to be completely dissociated in the vapour phase. These observations indicate that the stability order of the complexes is:

$$(CH_3)_2OBF_3 > (CH_3)_2SBF_3 > (CH_3)_2SBF_3.$$

It may be noted that volatility increases along this series, also indicative of decreasing stability, as mentioned in the Introduction. Thus the 0° saturation pressures of the complexes are 0.9 mm,⁽²¹⁾ 45.5 mm, and 398 mm, respectively.

⁽²⁰⁾ D. R. MARTIN and R. E. DIAL J. Amer. Chem. Soc. 72, 852 (1950).

^{*} It was earlier reported (A. B. BURG and A. A. GREEN J. Amer. Chem. Soc. 65, 1838 (1943)) that trimethylamine-boron trifluoride was undissociated at 230°, but this result was later corrected (A. B. BURG and C. L. RANDOLPH, unpublished). The form of the tensimeter used in the earlier work was not suited for studies at higher temperatures, and errors arose in correcting for the vapour pressure of mercury (A. B. BURG, private communication).

⁽¹⁸⁾ H. C. BROWN and R.H. HARRIS *ibid.* 71, 2751 (1949).

⁽¹⁹⁾ H. C. BROWN J. Chem. Soc. 1248 (1956).

⁽²¹⁾ H. C. BROWN and R. M. ADAMS *ibid.* 65, 2557 (1943).

With trimethylborine as the reference acid, the order of co-ordination in Group V is:(17, 19, 22)

$$(CH_3)_3 N \cdot B(CH_3)_3 > (CH_3)_3 P \cdot B(CH_3)_3 > (CH_3)_3 As \cdot B(CH_3)_3$$

The work with trimethylborine reported here was carried out in order to determine and clarify the order of co-ordination with Group-VI elements as ligands.

It was expected that the complexes of trimethylborine with Group VI ligands would be very weak, since alkyl groups on boron reduce its acceptor power.^(23, 10) This expectation was confirmed. It was found that dimethylether-trimethylborine was not formed at -78.5° , although dimethylsulphide and dimethylselenide both formed solid complexes at this temperature. In all three cases, dissociation was complete in the gas phase. Order of stability must therefore be inferred on the basis of saturation pressures, viz.:

$$(CH_3)_2$$
S·B $(CH_3)_3$ > $(CH_3)_2$ Se·B $(CH_3)_3$ > $(CH_3)_2$ O·B $(CH_3)_3$

It will be observed at once that this order is unusual. In analogy with boron trifluoride or trimethylaluminium, the expected order is O > S > Se, and even for trimethylgallium, the order is O > S. The unusual order can perhaps be understood in terms of two opposing effects: steric strain, brought about by interference between methyl groups on ligand and acceptor, which would be a maximum with dimethylether; and electron-pair donor power, which decreases with increasing size of the ligand. However, this is not necessarily the correct explanation for the anomalous order of co-ordination to trimethylborine. It may well be the result of those factors which may operate with borine itself, to be discussed below.

Orders of co-ordination with borine may now be compared. It was shown in the experimental part that dimethylsulphide-borine, which is only about 75 per cent dissociated in the gas phase at room temperature, is more stable than the dimethylselenide or dimethylether⁽²⁴⁾ complexes of diborane, both of which are completely dissociated in the gas phase. Thus, the order of co-ordination is:

$$(CH_3)_2S \cdot BH_3 > (CH_3)_2Se \cdot BH_3, (CH_3)_2O \cdot BH_3,$$

The relative order of the last two cannot be inferred from volatilities in this particular case. Although the selenium complex is less volatile, this may be due to its greater molecular weight. This is not a serious limitation, however, as the order S > O shows clearly enough that the order is anomalous when compared with boron trifluoride, trimethylaluminium, or trimethylgallium.

In passing, it may be mentioned that the new compounds described here with boron-selenium bonds imply the existence of a number of other boron-selenium compounds, which will probably have a similar relationship to the arsinoborines⁽²⁸⁾ as the thioborines⁽⁹⁾ have to the phosphinoborines.⁽²⁷⁾

It is interesting that towards both trimethylborine and borine the dimethyl compounds of the Group-VI elements have the same order of co-ordination, S > 0. However, towards the alkyls of the Group-V elements, trimethylborine has the same order of co-ordination as trimethylaluminium and trimethylgallium. Although

⁽²²⁾ See also results of H. C. BROWN discussed by J. CHATT J. Chem. Soc. 652 (1951).

 ⁽²³⁾ H. I. Schlesinger, N. W. Flodin, and A. B. Burg J. Amer. Chem. Soc. 61, 1078 (1939).
 ⁽²⁴⁾ H. I. Schlesinger, and A. B. Burg *ibid*. 60, 290 (1938); Chem. Rev. 31, 1 (1942).

 $(CH_3)_3$ N·B $(CH_3)_3$ ($\Delta H^\circ = 17.6$ kcal mole⁻¹)⁽¹⁷⁾ is only slightly more stable than $(CH_3)_3$ P·B $(CH_3)_3$ ($\Delta H^\circ = 16.5$ kcal mole⁻¹),⁽¹⁹⁾ the work of BROWN and his coworkers^(19, 25) has shown that the compound trimethylamine-trimethylborine is weakened appreciably by steric strain. The P-B bond is longer than the N-B bond so steric effects in $(CH_3)_3 P \cdot B(CH_3)_3$ would be less than in $(CH_3)_3 N \cdot B(CH_3)_3$.⁽²⁵⁾ Thus in the absence of steric factors $(CH_3)_3 N \cdot B(CH_3)_3$ would in all probability be appreciably more stable than $(CH_3)_3 P \cdot B(CH_3)_3$. This would be in agreement with expectations of normal (donor) σ -bonding. However, the rather similar stabilities of $(CH_3)_3$ N·B $(CH_3)_3$ and $(CH_3)_3$ P·B $(CH_3)_3$ may not be entirely due to steric factors.

The complexes formed by treating trimethyl compounds of most of the Group-V elements with diborane have been characterized by BURG et al. (26, 27, 28) The compounds trimethylamine-borine and trimethylphosphine-borine are exceedingly stable, essentially undissociated in the vapour at 200°. The compound trimethylarsine-borine must dissociate near 100°, since if heated at this temperature the pyrolysis products of diborane are quickly formed.⁽²⁸⁾ The order of bonding in Group V towards the reference acid borine is thus N, P > As, but because of the high stabilities of both trimethylamine-borine and trimethylphosphine-borine, it was not clear until this investigation whether the order of co-ordination was one paralleling that found for all other Group-III acceptor molecules so far investigated, namely N > P > Asor a new, hitherto unobserved order P > N > As.

The matter was resolved when it was shown that equilibrium in the reaction:

$$(CH_3)_3 N \cdot BH_3(s) + (CH_3)_3 P(g) = (CH_3)_3 P \cdot BH_3(s) + (CH_3)_3 N(g)$$

was about 80 per cent in favour of the products. Thus it may be concluded that:

$$(CH_3)_3P\cdot BH_3 > (CH_3)_3N\cdot BH_3 > (CH_3)_3As\cdot BH_3.$$

The anomalous orders of co-ordination to borine seem incapable of explanation on steric grounds. Steric effects in boron complexes should be more pronounced in the boron trifluoride series because of the larger size of the boron-trifluoride group,⁽²⁹⁾ and even more marked in the trimethylborine series. Yet the "normal" order of co-ordination is observed towards both boron trifluoride and trimethylborine in Group V, and in Group VI the expected order of co-ordination is found for boron trifluoride.

Attention may now be directed to a comparison of the relative strengths of complexes of borine and boron trifluoride. This is complicated by the dimerization of borine, a highly exothermic process which promotes the dissociation of borine complexes. An exact knowledge of the enthalpy change in the reaction:

$$B_2H_6(g) = 2BH_3(g)$$

would allow a quantitative comparison to be made, and for this reason the diboraneborine equilibrium assumes considerable importance. The first estimate of the energy required for the dissociation of one mole of diborane was apparently made by BELL and LONGUET-HIGGINS⁽³⁰⁾ who concluded that it involved absorption of at

⁽²⁵⁾ H. C. BROWN Record Chem. Progress (Kresge-Hooker Sci. Lib.) 14, 83, (1953).

 ⁽²⁶⁾ A. B. BURG and H. I. SCHLESINGER J. Amer. Chem. Soc. 59, 780 (1937).
 ⁽²⁷⁾ A. B. BURG and R. I. WAGNER *ibid.* 75, 3872 (1953).
 ⁽²⁸⁾ F. G. A. STONE and A. B. BURG *ibid.* 76, 386 (1954).
 ⁽²⁹⁾ H. C. BROWN and R. H. HOROWITZ *ibid.* 77, 1733 (1955).
 ⁽²⁰⁾ D. D. B. BURG *ibid.* 10, 277, 1034 (1954).

⁽³⁰⁾ R. P. BELL and H. C. LONGUET-HIGGINS Proc. Roy. Soc. A183, 357 (1945).

least 15 kcal. The diborane-borine equilibrium has recently received attention from BAUER and his co-workers⁽³¹⁾ who obtained the value $\Delta H^{\circ} = 28$ kcal mole⁻¹ by making a number of assumptions in the analysis of thermal and kinetic data.

It was found experimentally by $McCoy^{(31, 32)*}$ that for the reaction:

$$(CH_3)_3N(g) + 1/2B_2H_6(g) = (CH_3)_3N \cdot BH_3(g)$$

 $\Delta H^{\circ} = -17.3$ kcal mole⁻¹. This may be combined with ΔH° for the diboraneborine equilibrium to obtain:

$$(CH_3)_3 N \cdot BH_3(g) = (CH_3)_3 N(g) + BH_3(g)$$

with $\Delta H^{\circ} = 31.3$ kcal mole⁻¹. This value is to be compared with that for the dissociation:

$$(CH_3)_3 N \cdot BF_3(g) = (CH_3)_3 N(g) + BF_3(g)$$

for which ΔH° has been *estimated* as 26.6 kcal mole⁻¹. These values have led^{(31)*} to the conclusion that when trimethylamine in the reference base, boron trifluoride appears to be a weaker acid than borine by about 5 kcal.

It appears from more recent data that trimethylamine-boron trifluoride is more stable than this estimate implies. Thus LAWTON³³ has studied calorimetrically, in nitrobenzene, the reaction:

$$(CH_3)_3N(soln) + (CH_2)_5O BF_3(soln) = (CH_3)_3N BF_3(soln) + (CH_2)_5O(soln)$$

for which he found $\Delta H^{\circ} = -18.09$ kcal mole⁻¹. If this equation is now combined with the equation:

$$(CH_2)_5O(soln) + BF_3(soln) = (CH_2)_5O \cdot BF_3(soln)$$

also in nitrobenzene, for which $\Delta H^{\circ} = -12.8$ kcal mole⁻¹,⁽²⁾ the enthalpy change in the dissociation:

$$(CH_3)_3N \cdot BF_3(soln) = (CH_3)_3N(soln) + BF_3(soln)$$

may be evaluated as 30.9 kcal mole⁻¹.

If it is true, as preliminary results of BROWN⁽²⁾ seem to indicate, that the heats of formation of molecular addition compounds do not differ greatly in nitrobenzene solution and in the gas phase, it may be inferred that ΔH° for the gas-phase dissociation of trimethylamine-boron trifluoride is close to 30.9 kcal mole⁻¹ as well. Comparison with the bond strength of 31.3 kcal mole⁻¹ in trimethylamine-borine leads to the conclusion that there is little difference in the strength of attachment to trimethylamine. Indeed in the absence of steric effects, it is possible that boron trifluoride would be

 ⁽³¹⁾ A. SHEPP and S. H. BAUER J. Amer. Chem. Soc. 76, 265 (1954).
 (32) S. H. BAUER, A. SHEPP, and R. E. MCCOY *ibid.* 75, 1003 (1953).

⁽³³⁾ E. A. LAWTON, Ph.D. Thesis, Purdue University, 1952.

^{*} Since our paper was accepted for publication another paper by MCCOY and BAUER, J. Amer. Chem. Since on paper was accepted for paper distribution in order by the spectra of paper by matching to the determination of $\Delta H^{\circ} = 31.3$ kcal mole⁻¹ for the amine-adduct (CH₃)₃N·BH₃. Furthermore, the dissociation energy of diborane is now given as 28.5 \pm 2 kcal mole⁻¹. Originally a value of 32 kcal mole⁻¹ was reported ³² but see reference 31, and the list of revised thermodynamic data appended to the new paper (idem., loc. cit.)

revealed as the stronger acid towards trimethylamine. However, the relative acid strength of borine and boron trifluoride is not always the same, but is very dependent on the ligand. Thus it was shown that the displacement reaction:

$$CH_3)_3P \cdot BF_3(s) + 1/2B_2H_3(g) = (CH_3)_3P \cdot BH_3(s) + BF_3(g)$$

proceeded quantitatively to the right. Borine is thus more strongly bound than boron trifluoride to trimethylphosphine. Yet when $(CH_3)_3N\cdot BF_3$ was heated with diborane, using similar conditions, it was not possible to displace boron trifluoride. This indicates a greater stability difference in favour of the BH₃ adduct between $(CH_3)_3P\cdot BH_3$ and $(CH_3)_3P\cdot BF_3$ than between $(CH_3)_3N\cdot BH_3$ and $(CH_3)_3N\cdot BF_3$.

A rather similar variation of the order of acid strengths occurs in Group VI when oxygen and sulphur are the ligands. In the gas phase at ordinary temperatures, no interaction between dimethylether and diborane can be detected,⁽²⁴⁾ while the heat of dissociation of gaseous dimethylether-boron trifluoride is 13.3 kcal mole⁻¹.⁽²¹⁾ Dimethylsulphide-borine, on the other hand, was sufficiently stable for us to evaluate ΔH° for the reaction:

$$(CH_3)_2 S \cdot BH_3(g) = (CH_3)_2 S(g) + 1/2B_2 H_6(g)$$

as 5.2 kcal mole⁻¹, and ΔS° as 14.6 entropy units. Again we may utilize BAUER's^(31, 32) estimates for the diborane-borine equilibrium to obtain for the reaction:

$$(\mathrm{CH}_3)_2 \mathrm{S} \cdot \mathrm{BH}_3(g) = (\mathrm{CH}_3)_2 \mathrm{S}(g) + \mathrm{BH}_3(g)$$

the values $\Delta H^{\circ} = 19.2 \text{ kcal mole}^{-1}$ and $\Delta S^{\circ} = 31.7$ entropy units. This entropy increment is in reasonable agreement with the value 32.3 found⁽²¹⁾ for the reaction:

$$(CH_3)_2 O \cdot BF_3(g) = (CH_3)_2 O(g) + BH_3(g)_2$$

This agreement in the ΔS° values for the gas-phase dissociation of $(CH_3)_2 S \cdot BH_3$ and $(CH_3)_2 O \cdot BF_3$ supports the calculated ΔS° for the dissociation of diborane.⁽³¹⁾

It might be expected that dimethylsulphide-boron trifluoride would be even more stable than dimethylsulphide-borine, in analogy with the stabilities observed towards dimethylether. To the contrary, the stability of dimethylsulphide-boron trifluoride was found to be so low that it was not possible to determine ΔH° for its dissociation; at room temperature and 65 mm pressure, dissociation was more than 95 per cent complete. This fact indicates the much weaker character of boron trifluoride as an acid when dimethylsulphide is the ligand, and confirmation was further supplied when it was shown that the displacement reaction:

$$(CH_3)_2 S \cdot BF_3(l) + 1/2B_2H_6(g) = (CH_3)_2 S \cdot BH_3(l) + BF_3(g)$$

went about 80 per cent to the right.

Some results of H. C. $BROWN^{(19)}$ using pyridine (=Py) as the ligand are of interest in this discussion as well. If the rather large assumption is now made that the heat of dissociation of diborane is the same in nitrobenzene solution as in the gas phase, the following equations may be derived using BROWN's⁽¹⁹⁾ results, again assuming the correctness of the enthalpy change for the diborane-borine equilibrium:^(31, 32)

$$\begin{aligned} & \text{Py}(\textit{soln}) + \text{BH}_3(\textit{soln}) = \text{Py} \cdot \text{BH}_3(\textit{soln}) & \Delta H^\circ = -31.9 \text{ kcal} \\ & \text{Py}(\textit{soln}) + \text{BF}_3(\textit{soln}) = \text{Py} \cdot \text{BF}_3(\textit{soln}) & \Delta H^\circ = -25.0 \text{ kcal}.^{(2)} \end{aligned}$$

Thus, when pyridine is the reference base, it appears that borine exceeds boron trifluoride in bonding power. It is probably premature to arrive at a definite conclusion as to the exact acid strengths of BF_3 and BH_3 towards trimethylamine or dimethylether until more work is done. The data available so far indicate that acid strengths of BH_3 and BF_3 towards these ligands are rather similar. However it is clear from the work described here that borine bonds dimethylsulphide and trimethylphosphine better than does boron trifluoride.

It is convenient to summarize very briefly at this stage orders of co-ordination obtained here and elsewhere.^(4, 6, 19)

The observed orders of stability $(CH_3)_3P \cdot BH_3 > (CH_3)_3P \cdot BF_3$ and $(CH_3)_2S \cdot BH_3 > (CH_3)_2S \cdot BF_3$, as well as the existence of $OC \cdot BH_3$ and $F_3P \cdot BH_3^{(34)}$ and the nonexistence of $OC \cdot BF_3$ and $F_3P \cdot BF_3$, are unexpected in terms of electronegativity predictions. Attachment of electronegative groups to an acceptor atom often results in an increase of dative-bond strength. Thus the heats of dissociation of the following compounds decrease in the order $(CH_3)_3N \cdot BF_3 > (CH_3)_3$ $N \cdot B(CH_3)_2F > (CH_3)_3N \cdot B(CH_3)_2F > (CH_3)_3 \cdot B(CH_3)_3 \cdot (35)$ An increase in dative bond strength by substituting a more electronegative group on an acceptor atom is often offset, however, by other factors such as a change in the degree of availability of the vacant orbital on the acceptor atom, or perhaps the elimination of π -bonding which had been supplementing the simple dative σ -bond.

It is perhaps possible to account for the existence of OC·BH₃ and F_3P ·BH₃ and the nonexistence of their boron trifluoride analogues by asserting that the bonding is classical in nature and that borine is merely a more powerful electron-pair acceptor. It is certainly true that the acceptor power of boron trifluoride has in the past been overrated.^(36, 11)* Nevertheless it is rather unusual that when boron trifluoride and

⁽³⁴⁾ R. W. PARRY and T. C. BISSOT J. Amer. Chem. Soc. 78, 1524 (1956).

(35) A. B. BURG and A. A. GREEN ibid. 65, 1838 (1943).

(36) R. R. HOLMES and H. C. BROWN Abstracts of papers presented at the 129th meeting of the American Chemical Society, p. 28Q (1956).

^{*} Since our paper was accepted for publication in this journal, H. C. BROWN and R. R. HOLMES, J. Amer. Chem. Soc. 78, 2173 (1956), have determined the relative acid strengths of the boron trihalides, towards pyridine, as $BF_3 < BCI_3 < BBr_5$. This order is contrary to electronegativity expectations, but the weakness of BF_3 as an acid is interpreted (*idem.*, *loc. cit.*) in terms of $X - B \pi$ -bonding increasing along the series BBr₅, BCl₅, BF₅, thereby reducing the acceptor power of boron. Such an effect could also account for BF_3 having a rather similar acid strength to BH_3 towards (CH_3)₃N, but it does not explain the unusual orders of co-ordination shown by ligands of Groups V and VI towards BH_3 or the much greater stability of BH_3 adducts over their BF_3 adducts when the ligand has vacant orbitals. Furthermore, although pyridine is a base of low steric requirements, the presence of its π -orbitals might lead to complications in the N—B bond, the effect changing with different groups on boron.

borine form complexes with ligands that can only bond by means of a classical σ -dative bond the stabilities of their adducts are rather similar; yet with ligands possessing vacant orbitals of low energy, such as dimethylsulphide or trimethylphosphine, the stability of the borine complexes is greatly enhanced over their boron trifluoride analogues. Moreover, borine shows an unusual order of co-ordination towards the donor atoms of Groups V and VI, an order of co-ordination not shown by any other Group-III acceptor molecule so far investigated, except trimethylborine which parallels borine in Group VI. With borine, as for the sub-group elements investigated such as platinum,⁽³⁷⁾ sulphur is a better donor than oxygen and phosphorus better than nitrogen.

The unusual co-ordination chemistry of borine is difficult to understand in terms of a steric effect, since the steric requirement of boron trifluoride is larger than borine, yet boron trifluoride preserves orders of co-ordination towards the ligand atoms of both Group V and VI expected for classical dative bonding. Perhaps the behaviour of borine can be understood by extending a suggestion made by BURG et al.^(27, 28) to account for the unusual stability of certain phosphino- and arsino-borine polymers. Namely, that there may be a transfer of electron-density from B-H bonds to atoms bonded to boron having suitable vacant orbitals. Such behaviour may be of much more general occurrence in borine chemistry as a whole.

Indeed, it may be possible to treat the borine group in a borine complex like the methyl⁽³⁸⁾ group in organic chemistry, regarding the three hydrogen atoms as a pseudo-atom giving rise to a π -type orbital able to overlap empty orbitals, probably hybridized, provided by a suitable ligand atom. There might thus be a kind of $d_{\pi}-p_{\pi}$ bond in molecules like dimethylsulphide-borine, supplementing the classical dative σ -bond.

There is, however, an important difference between the effects postulated here and the "hyperconjugation" of organic chemistry. A charge separation occurs in a co-ordination compound like (CH₃)₂S-BH₃, which is very likely of a magnitude not usually encountered in organic chemistry. The drift of electron density from the borine group would lower the energy of the molecule not only by delocalization effects, but also by partial neutralization of the charge separation set up by the lonepair σ -bond.

It is necessary to postulate that a similar drift of electron-density does not occur from the BF₃ group, or that if it does occur is of too small a magnitude to influence chemical behaviour. This postulate is reasonable when the high electronegativity of fluorine is considered. Moreover, WALSH⁽³⁹⁾ considers that the weakness of the boron-hydrogen bond renders it unique in some ways, arguing that the electroncloud representing the bond is unusually diffuse.

A problem of long standing in the chemistry of the borine group is the existence of borine carbonyl.⁽⁴⁰⁾ A similar argument involving weak supplementary π -bonding with partial electron transfer from the B-H bonds to the vacant $2p_{\pi}$ orbital of carbon may account for the existence of OC·BH₃,⁽⁴¹⁾ and the apparent nonexistence of

⁽³⁷⁾ J. CHATT et al. J. Chem. Soc. 652 (1951); 2787, 4461 (1955).
(38) C. A. COULSON Quart. Rev. 1, 144 (1947).
(39) A. D. WALSH in Victor Henri Memorial Volume, Contribution to the Study of Molecular Structure. DeSoer, Liege (1947) pp. 191-199.
(40) A. B. BURG and H. I. SCHLESINGER J. Amer. Chem. Soc. 59, 780 (1937).
(41) A. B. BURG Record Chem. Progress (Kresge-Hooker Sci. Lib.) 15, 159 (1954).

OC·BF₃. Borine carbonyl has a low dipole moment and an HBH angle near 114°,⁽⁴²⁾ larger than that expected for tetrahedral boron, so the bonding may be somewhat like the multiple bonding in nickel carbonyl with the same effect on volatility.

There has been some difference of opinion as to the correct single-bond radius of the boron atom which perhaps renders unsatisfactory the deduction of the order of the boron-carbon bond from the observed bond distance. It is an experimental fact, however, that the boron-carbon distance in borine carbonyl is 1.540 Å,⁽⁴²⁾ in agreement with the corresponding distance in trimethylborine.⁽⁴³⁾ MULLIKEN⁽⁴⁴⁾ considers that the latter molecule is strongly stabilized by hyperconjugation. It may not be correct to assume that borine carbonyl is adequately described in terms of a $C \rightarrow B$ classical dative bond so weak that it fails to pull the boron atom very far out of the planar sp²-arrangement.

Similarly, the recently discovered F₃P·BH₃⁽³⁴⁾ may owe its existence to supplementary π -bonding involving overlap of the vacant 3*d*-orbitals of phosphorus and the pseudo π -orbital provided by the hydrogen atoms on boron. It is significant that phosphorus trifluoride does not bond other Group-III acceptor molecules, like boron trifluoride, yet it does form complexes with some of the subgroup elements, e.g., $Ni(PF_3)_4$,⁽⁴⁵⁾ where the bonding is believed to be multiple in character. It is true that the bonds in OC·BH₃ and F₃P·BH₃ are weak, but it should not be concluded that these molecules are adequately described in terms of the classical co-ordinate link on this account. It is significant that NF₃ does not add to the BH₃ group.⁽³⁴⁾ This is to be expected if the ideas presented here are correct. Although nitrogen is a superior electron-pair donor to phosphorus, the adduct $F_3N \cdot BH_3$ might not exist because nitrogen has no orbitals above the $2sp^3$ -octet suitable for chemical bonding. No supplementary π -bonding is possible, and the only bonding mechanism is a classical $N \rightarrow B$ dative bond weakened by the electronegative fluorine atoms. In $F_3P \cdot BH_3$, the σ -dative bond is also weakened by the fluorine on phosphorus, but dative π -bonding is now possible and indeed enhanced by the fluorine atoms.

In conclusion, it seems appropriate to quote from MULLIKEN:⁽⁴⁶⁾

"However, it must be kept in mind that the strength of a (Lewis) acid is not quite a unique absolute quantity, but depends appreciably on specific features of its interaction with the base with which it is paired."

Acknowledgement—It is a pleasure to acknowledge the generous support of this work by the United States Office of Naval Research.

⁽⁴²⁾ W. GORDY, H. RING, and A. B. BURG Phys. Rev. 78, 512 (1950).

 ⁽⁴³⁾ H. A. LEVI and L. O. BROCKWAY J. Amer. Chem. Soc. 59, 2085 (1937).
 (44) R. S. MULLIKEN Chem. Rev. 41, 207 (1947).

 ⁽⁴⁵⁾ G. WILKINSON J. Amer. Chem. Soc. 73, 5501 (1951).
 (46) R. S. MULLIKEN *ibid.* 74, 811 (1952).